



Solid state storage of hydrogen and its isotopes: An engineering overview

Rupsha Bhattacharyya*, Sadhana Mohan

Heavy Water Division, Bhabha Atomic Research Centre, Mumbai 400085, India



ARTICLE INFO

Article history:

Received 25 February 2014

Received in revised form

4 August 2014

Accepted 3 September 2014

Keywords:

Metal hydride

Reversible storage

Storage bed

Hydrogen storage

ABSTRACT

Solid state storage of hydrogen in the form of a reversible metal or alloy hydride has been proven to be a very effective and compact way of storing hydrogen and its isotopes for both stationary and mobile applications. Other than metal based systems, a wide variety of materials have been studied for this purpose and their thermodynamic properties, storage capacity, etc. have been determined. Heat transfer issues form an important consideration for the engineering design of a metal hydride based hydrogen storage system, hence several kinds of storage beds have been fabricated and their performance analyzed. The kinetics and mechanism of these hydriding processes for various types of storage materials have also attracted a great deal of interest. This work summarizes some of the information available on solid state storage of hydrogen isotopes which is essential for the engineering design of a storage system. The focus is on the engineering and technical issues and the practical considerations pertinent to the design and operation of such storage systems for various applications.

© 2014 Elsevier Ltd. All rights reserved.

Contents

| | |
|--|-----|
| 1. Introduction..... | 872 |
| 2. Classes of materials for hydrogen storage | 873 |
| 2.1. Heavy metals and their alloys..... | 873 |
| 2.2. Carbon based materials..... | 875 |
| 2.3. Nitrogen, boron, lithium, aluminum and magnesium based materials..... | 875 |
| 2.4. Metal organic frameworks (MOFs)..... | 876 |
| 2.5. Zeolites..... | 876 |
| 3. Thermal issues in solid state hydrogen storage systems..... | 876 |
| 4. Design of storage beds for hydrogen isotopes | 877 |
| 4.1. General considerations | 878 |
| 4.2. Bed heating and cooling arrangements | 878 |
| 5. Kinetic models of hydriding and dehydriding reactions | 879 |
| 6. Technological difficulties in solid state hydrogen storage | 879 |
| 7. Computational models of solid state hydrogen storage beds | 880 |
| 8. Summary and conclusions | 881 |
| References | 881 |

1. Introduction

Hydrogen is often described as being the fuel of the future [1]. For widespread use of hydrogen in place of the more traditional fossil fuels, it is imperative to have very efficient storage and transportation systems for it. Use of metal getter beds is one of

* Corresponding author. Tel.: +91 22 2559 2962.

E-mail address: rupshabhattacharyya1986@gmail.com (R. Bhattacharyya).

Nomenclature

| | | | |
|----------|---|----------------|---|
| A_B | Van't Hoff constants for equilibrium temperature-pressure relation, dimensionless and K^{-1} respectively | K | permeability, m^2 |
| A_h | convective heat transfer area available in the bed, m^2 | \dot{m} | reaction rate, $kg\ m^{-3}\ s^{-1}$ |
| c | density of solid at any time, $kg\ m^{-3}$ | M_g | molecular weight of hydrogen (or its isotope), $gm\ mol^{-1}$ |
| C_{Pg} | specific heat capacity of the gas, $J\ kg^{-1}\ K^{-1}$ | m_s | mass of solid, kg |
| C_{Ps} | specific heat capacity of the solid, $J\ kg^{-1}\ K^{-1}$ | P | hydrogen pressure, Pa |
| c_{SS} | density of fully hydrided or saturated solid, $kg\ m^{-3}$ | P_{eq} | equilibrium pressure of hydrogen over metal hydride, Pa |
| d_p | diameter of catalyst, m | R | universal gas constant, $8.314\ J\ mol^{-1}\ K^{-1}$ |
| E_a | activation energy of the hydriding reaction, kJ/mol | t | time, s |
| E_d | activation energy of the dehydriding reaction, kJ/mol | T_g | absolute gas temperature, K |
| h_{sg} | convective heat transfer coefficient from hydrogen to solid phase, $W\ m^{-2}\ K^{-1}$ | T_S | absolute solid temperature, K |
| H | enthalpy of hydriding reaction, $J\ mol^{-1}\ K^{-1}$ | v_g | superficial velocity of gas in the porous bed, $m\ s^{-1}$ |
| k_a | frequency factor for hydriding reaction, s^{-1} | V_S | volume of solid in the getter bed, m^3 |
| k_d | frequency factor for dehydriding reaction, s^{-1} | ϵ | void fraction in the hydride bed, dimensionless |
| k_e | effective thermal conductivity of the porous solid, $W\ m^{-1}\ K^{-1}$ | μ | gas viscosity, $Pa\ s$ |
| k_g | thermal conductivity of hydrogen, $W\ m^{-1}\ K^{-1}$ | $(\rho C_p)_e$ | effective specific heat capacity of the hydrogen–metal hydride system, $J\ kg^{-1}\ K^{-1}$ |
| k_s | thermal conductivity of the metal/metal hydride, $W\ m^{-1}\ K^{-1}$ | ρ_s | solid density, $kg\ m^{-3}$ |
| | | ρ_g | gas density, $kg\ m^{-3}$ |

the most viable options for both short and long term storages and handling of hydrogen and its isotopes. This applies to stationary systems like laboratories, fusion energy research centers as well as mobile systems like automobiles, mining vehicles, and submarines and so on. The adsorbed hydrogen (or its isotopes D, T) on a metal or alloy M forms MH_3 (or MD_3 or MT_3) by chemisorption. MH_3 is dissociated by heating and hydrogen is liberated from the solid phase. On cooling, the metal or alloy quickly reabsorbs the hydrogen gas [2]. This reversible liberation and uptake of hydrogen or deuterium or tritium from getter beds can be performed many times under appropriate conditions depending on the type of material chosen without loss of efficiency. These properties of the metal hydrides or metal tritides make them excellent hydrogen/tritium storage and pumping materials. The major advantage of this route of hydrogen storage is that a large amount of gas can be stored in a very small volume when compared to traditional hydrogen storage methods involving compressed gas cylinders or cryogenic storage of liquid hydrogen, and once hydrogen is recovered from the adsorbent bed, it is of a very high purity as well [3].

Despite all the advantages mentioned above the actual design of a solid state hydrogen storage system presents several engineering challenges mainly in the form of heat transfer issues, poor chemical kinetics and the formation of possible explosive reaction mixtures with oxygen and moisture, low gravimetric storage capacity of many materials, powder formation and volume expansion of the storage material during hydriding, fatigue based deformation of the bed under cyclic pressure changes and thermal loads, as well as safety issues on account of the toxic and pyrophoric nature of many storage materials. No one material offers the best set of thermodynamic and kinetic properties, but it is often possible to engineer the storage system in such a way that an optimal design is obtained for a chosen storage material. It must be mentioned that the choice of materials as well as the ultimate system design is mainly governed by the intended application, whether it is onboard storage for vehicular applications which must necessarily be more compact or land based tritium storage and delivery system where the space constraint often arises from the need to handle all tritium based systems inside fume hoods or glove boxes. Thus different system designs have been proposed and they have their own merits and demerits.

This paper presents a brief overview about various kinds of hydrogen storage materials developed and studied, with greater focus on the design considerations for the storage vessels, the heat and mass transfer aspects of storage and the computational models developed to study the behavior of these beds. Most of the practical applications have been based on metal based systems and this review places emphasis on the various issues pertinent to such systems.

2. Classes of materials for hydrogen storage

The desirable properties of a storage material for hydrogen are generally stated to be high gravimetric and volumetric capacity, reversibility of hydriding and dehydriding steps, favorable equilibrium temperature–pressure characteristics, adequate stability of the hydride formed and low sensitivity to impurities present in feed gas. All the desired properties are yet to be found in one single material even after decades of research in this field. Researchers have examined several classes of materials for solid state hydrogen storage. The two major routes by which hydrogen is immobilized in a solid matrix are (i) the physical adsorption of hydrogen on the storage material or (ii) the dissociative chemisorption of hydrogen gas and diffusion of atomic hydrogen in the solid matrix, under appropriate conditions of temperature and pressure. The major groups of materials are briefly reviewed and compared in the following sections. More detailed and comprehensive reviews of the materials aspects have already been published, some of the more recent ones being the one by Dalebrook et al. [37], by Durbin et al. [3] and Lototskyy et al. [151].

2.1. Heavy metals and their alloys

Storage of hydrogen isotopes as a metal hydride, deuteride or tritide is one of the most common methods adopted in laboratories and especially in tritium handling facilities the world over [4,5]. Several heavy metals especially transition metals and rare earths and more commonly their binary, ternary and more complex alloys have been studied and their thermodynamic and kinetic behavior evaluated [6–9]. These alloys are generally represented as AB, AB_5

or AB_2 [10]. Detailed studies have been performed for many of these metals and alloys, though all the necessary information for the design of an actual system may not be available for all of them [11], particularly kinetic data for reactor design, data pertaining to thermal cycling behavior of the materials and thermal and transport properties. Calculated and experimental values of the heat of hydriding reactions with several transition metals and their binary alloys are presented by Miedema et al. [12], while Van't Hoff plots (i.e. equilibrium pressure-temperature graphs) for various other alloys are also presented elsewhere [13–15]. Some of the most widely studied materials, both from a materials characterization point of view and systems engineering aspect include uranium, zirconium cobalt (ZrCo), titanium, lanthanum nickel (LaNi_5), ZrFe , ZrNi and some others. Much useful information about them has been summarized by several authors [10,11,16]. While the uptake process is generally spontaneous at ambient conditions and the release also does not need infeasible conditions for many such alloys, the major problem in their usage is the low gravimetric storage density exhibited by them (about 2–3% by weight only). These materials have generally not been considered for mobile applications but their proposed usage is primarily for the nuclear industry.

For tritium storage requirements in fusion energy research, uranium and ZrCo have been identified as reference materials and therefore they have been widely studied and compared [17,18]. Table 1 presents a comparison of these two candidate materials for tritium storage in fusion research facilities.

Depleted uranium is available in the nuclear industries but it is still a regulated material and it may not be easily available everywhere. Moreover there are some other problems with the handling of uranium, viz. uranium powder is pyrophoric, the generation of significant tritium pressure requires a high temperature that results in permeation of tritium through the vessel wall and the storage capacity is also permanently reduced by exposure to reactive impurity gases [18]. Uranium is generally used in powder form since powder would offer higher surface area for adsorption but very fine powders also have greater pyrophoric characteristics. Experimental observations suggest that spherical particles of uranium having a size greater than 1/16 in. will not spontaneously ignite in air [19].

Out of numerous binary alloys of metals examined for hydrogen isotope storage, especially in the field of fusion research, ZrCo is possibly the one whose thermodynamic properties with respect to hydrogen storage are closest to those of uranium. Hence there is an increasing interest in studying this material further. Unlike

other metal combinations (e.g. La-Ni-Al), ZrCo has low level of toxicity and does not need to be refrigerated for hydrogen isotope storage [18].

For long term storage of tritium when frequent recovery and delivery of the gas are not needed, titanium has been envisaged as a good material. Titanium is an inexpensive metal that can absorb and store tritium in a compact solid form at a pressure of approximately 1.33×10^{-7} mbar at room temperature. It is used as a storage medium for long periods and retains helium from tritium decay to a concentration of 0.3–1 atom of helium on titanium atoms. Titanium tritide is very stable, even when exposed to air and is much less pyrophoric compared to the parent metal. But it is difficult to recover stored tritium on titanium bed than on other metals, it being necessary to provide a large amount of heat for desorption. Unlike depleted uranium which produces very fine particles upon repeated hydriding and dehydriding which are pyrophoric in air, titanium sponge is not expected to be so reactive in the presence of moisture and air under typical storage conditions. Since titanium powder does not react with hydrogen or its isotopes at room temperatures, it has to be activated by heating to 500 °C under vacuum conditions (typically 10^{-6} Torr) so that the surface impurity layers, mainly oxide layers get dissolved in the bulk material, thus making pure metal surface available for hydriding. In this respect it is similar to uranium or ZrCo as getter material. Activation temperature has been shown to have a strong influence on the adsorption properties of sponge titanium. Typically 3–4 h are needed for the activation. This time is somewhat higher than the time required for activating depleted uranium or ZrCo beds. The dehydriding temperatures examined are typically around 550–600 °C. This is somewhat higher than the typical desorption temperatures for uranium or ZrCo . The heat released is 80–160 kJ/mol of hydrogen adsorbed. This figure is somewhat higher than that for uranium or ZrCo . Titanium sponge is much less dense as compared to uranium powder, its density being around 1–1.5 kg/l [20,21].

The hydrogen adsorption properties of palladium have been well known for a long time [126]. Experimental characterization of the thermodynamics of the hydrogen-palladium system has been performed [127]. The recent focus is on the use of palladium for hydrogen storage in nanoparticle form as opposed to bulk form [128–130] or as a modifying agent for other classes of materials like carbon nanotubes and graphenes [131–136]. Palladium by itself has been used at various facilities handling tritium for storage purposes but it suffers from the disadvantage of low gravimetric loading

Table 1
Comparison of ZrCo and uranium as getter materials for hydrogen/tritium storage [17,18].

| Point of comparison | Depleted uranium versus ZrCo alloy |
|---|---|
| Pyrophoric nature | Uranium powder is much more pyrophoric in air at room temperature than ZrCo powder. |
| Radioactive characteristics | Uranium powder handling is more difficult because of its radioactive nature, unlike ZrCo . |
| Volume expansion on hydride formation | Uranium expands by about 75% on hydriding whereas ZrCo expands by about 15–20%. |
| Powder formation | ZrCo powder is more difficult to contain than uranium dust. |
| Reaction kinetics | Under identical conditions, uranium absorbs hydrogen faster than ZrCo and is less sensitive to initial hydrogen content in the solid. Desorption rate of hydrogen from ZrCo is slower. |
| Heat release during adsorption/reaction | Heat release during hydriding is 85 kJ/mol protium for uranium whereas it is 97.5 kJ/mol T_2 for ZrCo . |
| Reactions with impurities | ZrCo is much less sensitive to the presence of impurities like oxygen, nitrogen or methane in the hydrogen/tritium stream than uranium. |
| Disproportionation reaction | Zr undergoes disproportionation reaction at temperatures above 350 °C and high hydrogen pressure ($(\text{ZrCo})_x = 0.5\text{Zr}T_2 + 0.5\text{ZrCo}_2 + 0.5*(1-x)T_2$). Uranium exhibits no such reactions during dehydriding. |
| Hydrogen dissociation pressure | The hydrogen equilibrium pressure over ZrCo hydride at room temperature is higher than that over uranium hydride. |
| Structural changes on hydriding | There is structural change in ZrCo from bcc to orthorhombic on hydriding. No such structural change is observed in uranium. |
| Hydriding and dehydriding temperatures | Hydriding of both materials can be carried out at room temperature. For dehydriding of uranium temperature around 430 °C and for ZrCo temperature around 350 °C have been recommended. |
| Availability | Depleted uranium is more readily available than the specially synthesized alloy ZrCo . |
| Storage capacity | The storage capacity of ZrCo is about 247.5 l/kg and that of uranium is 156.1 l/kg under standard temperature and pressure. |

capacity i.e. the maximum palladium to hydrogen or tritium ratio (on atom basis) is about 0.7 as compared to about 3.0 for uranium or even ZrCo. But the advantage that palladium offers is the relatively low temperature of 350 °C at which palladium hydride can be regenerated and the fact that palladium powder is not pyrophoric which makes its handling easier [137]. The lower regeneration temperature is a marked advantage of palladium as compared with uranium or titanium.

2.2. Carbon based materials

Several carbon based substrates like porous carbon and carbon nanotubes and nanofibres of various structures have been studied for their hydrogen storage properties. It was first reported by Dillon et al. that single walled carbon nanotubes having diameter of the order of a few nanometers allows hydrogen gas to condense to a high density of about 5–10% by weight inside it, thus leading to very high hydrogen adsorption by this class of materials [22]. Cheng et al. summarize storage capacity data from various sources along with storage temperature and pressure for several kinds of carbon nanotubes. There is considerable variation in the data from various groups of researchers, thus obtaining reproducible results from adsorption experiments is an issue with nanotube materials. The structure of the nanotubes (i.e. whether they are single walled or multi-walled or in the form of fibers or ropes, presence of other elements or doping agents like lithium or potassium, etc.) affects the hydrogen uptake properties [23]. The promising feature noted from the experiments reported is that the adsorption takes place quite effectively even at room temperature and also moderate pressures (about 1–10 bar), though in some instances much higher storage capacities are reported for higher filling pressures of hydrogen. Hydrogen release temperatures range from 300 K to 600 K depending on the nature of the nanotubes [24]. It has also been suggested that the technique of reactive ball milling of the carbon nanotube material in hydrogen atmosphere for prolonged duration result in higher hydrogen adsorption [24]. But the general view about hydrogen storage in nanotubes is that while surprisingly high uptake capacities have been reported in several cases, these data may not always be very reliable or reproducible and the use of carbon nanotubes may not be a very efficient way of storing hydrogen, given the low or even cryogenic temperature and high pressures needed for a meaningful gravimetric hydrogen storage density to be achieved. Moreover, cost considerations and the lack of appropriate technologies for large scale production of carbon nanostructures are also deterrents in their use as hydrogen storage material.

While carbon based materials may not actually prove to be very useful for storage purposes, they play an important role as a material of construction in the form of carbon fibers which are about 10 times stronger than steel. These fibers are used to reinforce tanks for compressed hydrogen storage at pressures of about 650 bar. The resultant structure is much lighter in weight than an equivalent all-steel structure [34].

Activated carbon is one well-known material for adsorption of hydrogen, especially under cryogenic conditions and high hydrogen pressure (typically at temperatures of 77 K). The chemical treatment carried out to prepare the activated carbon governs its porosity and surface properties, thus directly affecting its hydrogen storage behavior [138,139]. Doping of the carbon sites by various elements or the presence of elements like oxygen have also been shown to have only a negligible effect on the hydrogen uptake characteristics and the high available surface area for hydrogen adsorption is generally accepted as the main reason for it to be considered as a hydrogen storage material [140,141]. The typical adsorption capacities by weight percentage reported for activated carbon range from 1% to 7% at 77 K and pressures of 1–20 bar respectively. At

pressures slightly above ambient (viz. 2–4 bar), the gravimetric capacities reported are about 2–3% which is only slightly greater than that available from metal and alloy systems. Additionally cryogenic conditions have to be maintained to enable the use of activated carbon for hydrogen adsorption and storage. Recovery of stored hydrogen at ambient temperatures is possible but the storage behavior of these materials is not very conducive for the design of compact systems having ease of operation.

2.3. Nitrogen, boron, lithium, aluminum and magnesium based materials

Many light element compounds are known that have high gravimetric hydrogen capacities. However, most of these materials are thermodynamically too stable, and they release and store hydrogen much too slowly to be useful for practical use. New light element chemical systems involving strategies like destabilization have been developed by some researchers that have high hydrogen capacities while also having thermodynamic properties better suited for hydrogen storage applications [25].

Boron and nitrogen based materials have been studied for their hydrogen storage capacities in connection with the operation of PEM fuel cells, though not as such in the nuclear fusion context [26]. These materials are often referred to as chemical hydrogen storage materials or chemical hydrides [34]. Boron compounds like sodium or lithium borohydrides and ammonia borane as well as nitrogen compounds like ammonia, lithium amide, and hydrazine have been quite widely studied mainly in the context of onboard storage of hydrogen for automobile applications [26]. These materials while showing some of the highest hydrogen capacities suffer from the disadvantage of being extremely stable compound, therefore high temperatures of around 600–900 K, as also the use of catalysts is required to dissociate them. Various details regarding their use, storage capacity, dissociation properties and synthesis have been provided elsewhere [26]. Since a large variety of these complex hydrides as well as destabilized hydrides have been synthesized and studied for the storage applications, it is necessary to have some guidelines for selecting some materials for a particular purpose are also required, which have been provided based on thermodynamic criteria [27].

Magnesium and aluminum based hydrides (i.e. alanates) have also been studied extensively and a great deal of effort has been made to improve their thermodynamic characteristics, hydrogen adsorption kinetics and long term usability after several cycles of hydriding and dehydriding by the addition of other elements in a way similar to destabilization of boron based hydrides [28,152]. A number of comprehensive reviews of these materials have been published, with information about the most pertinent thermodynamic and kinetic parameters for storage. Out of these, magnesium based compounds and titanium or zirconium doped sodium alanates (doped NaAlH₆) appear quite promising [28,29,34–36]. A review of the properties of sodium alanate based systems, with focus on how doping improves the thermodynamic and kinetic properties of these substances with respect to hydrogen storage has been recently published [150,151]. The prospects of aluminum hydride itself as a material for hydrogen storage have been discussed thoroughly elsewhere [153]. Unlike many of the heavy metal hydrides, these lighter element hydrides show high gravimetric storage capacity but the major issue with their use is the requirement of high temperature even for the adsorption step, not to mention the desorption step, though in many cases the temperature for desorption is somewhat lower than that for the heavy metal hydrides. Even if adsorption is possible at ambient conditions, the stability of these materials under thermal cycling and the retention of the uptake capacity after a given number of cycles are often in question [28]. Moreover finding suitable structural

materials for fabricating the bed is an issue with the high temperature hydrides, since there may be solid-state interactions and phase change reactions between the storage and the construction materials. But even after an enormous amount of research work dedicated to these materials there is yet to be found one or even one limited set of materials having all desirable attributes for hydrogen storage applications.

2.4. Metal organic frameworks (MOFs)

Metal organic frameworks represent a class of materials which are capable of storing significant quantities of hydrogen in a physically adsorbed form. These are chemical compounds having a metal ion or ions which are coordinated with an organic molecule and the structure of these compounds is porous. This porous framework offers a large specific surface area for hydrogen adsorption, thereby acting as a storage medium. These properties were first reported about a decade back for MOF-5 (having composition of $Zn_4O(BDC)_3$, BDC being 1,4-benzenedicarboxylate) under both ambient and cryogenic conditions. It was seen that this material could adsorb up to 4.5 wt% of hydrogen at cryogenic conditions and 1 bar pressure and 1% under ambient conditions with pressure being 20 bar [30]. Subsequently several different frameworks have been studied, the thermodynamic properties like heat of adsorption have been evaluated and theoretical modeling of the hydrogen uptake behavior of these materials have been undertaken [31,32]. The high surface area available in these structures and the possibility of improving the hydrogen storage behavior of these materials through the introduction of other metal ions like Li^+ , Cu^{2+} , Mg^{2+} , etc. have led to extensive research work (synthesis, characterization and study of hydrogen uptake) involving MOFs [32]. It has been demonstrated theoretically by considering around 4000 MOF species that the species with specific surface of 3100–4800 $m^2 g^{-1}$ have the maximum volumetric hydrogen storage capacity and further increase of surface area does not appreciably increase storage performance [154]. This enables researchers to focus on those MOFs with surface areas in this range and improve their other properties by suitable techniques like adequate mechanical strength of the MOF structure and thermodynamic properties. The introduction of more polarized links and reduction in pore dimensions in the MOF has been shown to have positive effect on its hydrogen adsorption capacity [155]. The generally accepted mechanism of hydrogen uptake by MOF is the polarization of the hydrogen molecule by the metals present in the framework and its electrostatic stabilization [156]. Dissociative chemisorption of hydrogen on to the porous network has been thought of as a potential method to increase the hydrogen uptake capacity of MOFs and this has mechanism has shown to enhance the storage capacity of MOF-5 and IRMOF-8 by 8 times [32,157]. The major issue with them, as with carbon nanotubes, is the requirement of cryogenic conditions and high hydrogen pressure to achieve the high gravimetric and volumetric storage. Thus it is necessary to find suitable agents (metal ions, etc.) that could modify MOF properties favorably and allow hydrogen to be stored in them under ambient conditions of temperature and moderate hydrogen pressure (e.g. up to 10 bar).

2.5. Zeolites

Zeolites are crystalline alumino-silicate materials having highly ordered structures and uniform pore sizes. They have proven to be good adsorbents for various gases like hydrogen, moisture, carbon dioxide, etc. Study of these materials for hydrogen storage applications is a logical extension [142–149]. At high pressures (up to 900 bar) and high temperatures (up to 350 °C) hydrogen can be

forced into the porous structure of zeolites where it can remain confined even when room temperature conditions are maintained [143]. This mechanism of hydrogen loading is termed encapsulation and it is highly dependent on the pressure, temperature and nature of cations present in the zeolite framework. By the mechanism of encapsulation, it has been observed that only a low gravimetric loading is achieved, even at high pressures of hydrogen, ranging from 0.1% to 0.6% by weight. The other mechanism of hydrogen storage is physisorption and this is accomplished at cryogenic temperatures (e.g. 77 K) only with low hydrogen pressures [143]. The adsorption capacity is dependent on the pore size in the zeolite network. At 77 K and 40 bar pressure, a maximum loading capacity of 2.55% by weight has been observed for NaX zeolites [144,145]. The physisorption adsorption capacities have been explained through the Langmuir adsorption model which assumes that a monolayer of the gas forms on the available sites for storage. Improvements in room temperature hydrogen storage have been achieved through the doping of the zeolite structure with palladium and similar metals [148]. Bridging techniques and the mechanism of spillover have been used to enhance hydrogen uptake in zeolites in low and ambient temperature conditions [146]. The available surface area for adsorption is quite strongly correlated to the ultimate storage capacity when physisorption is the dominant mechanism of hydrogen uptake [147]. Apart from zeolites, various other nanoporous materials for hydrogen storage have also been studied recently, especially for larger pore sizes [149]. It has been seen in these studies that hydrogen uptake decreases with increase in pore size of the solid matrix, thus showing the importance of surface area of the medium in taking up hydrogen and retaining it.

The hydrogen storage and release properties of the various candidate materials as discussed above are summarized and compared in Table 2.

3. Thermal issues in solid state hydrogen storage systems

The solid state storage of hydrogen in the form of various hydrides or physically adsorbed forms is accompanied by exothermic adsorption based phase change processes while recovery is an endothermic process [33]. From the brief discussion about the major classes of solid materials studied for hydrogen storage applications, it is very clear that efficient heat removal during the adsorption step and heat supply during recovery of the adsorbed hydrogen are the major areas of engineering research pertinent to solid state hydrogen storage. Thus knowledge about the thermodynamic properties (heat of reaction, equilibrium pressure versus temperature relation for a given material) and thermal properties (thermal conductivity, heat capacity) as well as adsorption or reaction kinetics is necessary in order to design a system for hydrogen storage [33]. For hydrogen based vehicular applications, it has been estimated that the average cooling requirement during hydrogen charging or adsorption is about 0.7 MW [33]. This shows the importance of having an efficient cooling system alongside the storage bed. Similarly during dehydriding there is an equivalent heating requirement for the bed. Thus the provision of heating and cooling arrangements along with the arrangement to contain the storage medium suitably is an integral part of the system design.

During adsorption there is a need to remove heat from the bed, so that nearly isothermal conditions can be obtained and advantage can be taken of the bed material's high reversible adsorption capacity at lower temperatures for all kinds of solid state storage systems. The rate of heat loss to the ambient (by mechanisms like radiation and/or natural convection) or to a cooling fluid circulated outside the bed or conditions like hot spot formation is primarily governed by the effective thermal conductivity of the metal hydride powder i.e. conduction through the gas-solid bed matrix is the main heat transfer

Table 2

Summary of hydrogen storage properties of various classes of materials.

| Material | Typical form | Advantages | Disadvantages |
|--------------------------|--|---|---|
| Metals | Uranium turnings/powder | Fast kinetics, hydrogen uptake at ambient temperature and pressure possible with powder, favorable thermodynamic properties, widely studied and used for storage | Radioactive material, toxic, pyrophoric in powder form, susceptible to poisoning by O ₂ , N ₂ , large volumetric expansion on hydriding |
| | Titanium pellets/sponge | No reaction with ambient air, much less pyrophoric compared to uranium, not radioactive | Relatively high regeneration temperature for hydrogen recovery, so suitable for long term storage, lower storage capacity compared to uranium |
| | Palladium powder | Not radioactive or pyrophoric even in powder form, relatively low regeneration temperature for hydrogen recovery | Low gravimetric storage density among metals |
| Metal alloys | Powder/chips/pellets | Tunable hydrogen storage properties depending on metals present in alloy, wide variety of metal combinations can be used | Special synthesis techniques needed for each alloy |
| Carbon | Porous carbon, activated carbon, nanotubes, fibers | Opportunity of tuning storage properties by changing synthesis techniques and adding doping elements like palladium, recovery of hydrogen at ambient conditions possible | All usable forms have to be specially synthesized and treated, high pressure and cryogenic temperature of hydrogen needed to load appreciable amounts of hydrogen on carbon |
| Light elements | Chemical hydrides of N, Li, Al, Na, B | High gravimetric density of hydrogen as compared to heavy metal based systems, property tuning possible and destabilization techniques can be applied to improve thermodynamic properties | Most compounds are thermodynamically too stable, very slow kinetics of hydriding and dehydriding, high temperature and pressure needed |
| Metal organic frameworks | Crystalline powder | High surface area and pore volume allow hydrogen to be physically adsorbed, recovery at ambient temperature possible, fast kinetics, durability over many cycles | High pressure and cryogenic temperature of hydrogen needed to load appreciable amounts of hydrogen on carbon, have to be synthesized specially, loss of surface area on exposure to air |
| Zeolites | Beads/pellets | High surface area and pore volume allow hydrogen to be physically adsorbed, gas recovery at ambient temperature or above ambient temperature possible, much less expensive compared to any other material | High pressure and cryogenic temperature of hydrogen needed to load appreciable amounts of hydrogen on carbon |

mechanism at work [38]. The effective thermal conductivity of the powder is quite low, typically lying in the range of 0.5–2 W/mK for a wide variety of metal hydrides [33]. There are various factors on which the value of effective thermal conductivity depends, mainly the pressure of the gas in the pores, the particle size, bed porosity or void fraction and there are a variety of correlations proposed in literature to calculate the thermal conductivity of metal hydride beds based on these parameters [39,40,113]. But most of these correlations assume a mono-disperse particle size distribution and the range of particle sizes examined to arrive at these correlations are larger (in the range of millimeters) than the powder particle sizes (in the range of 10–50 micron) in typical well activated metal hydride beds. In the absence of data about a given system this range of values can be used as an approximation. Several specific studies pertaining to the characterization of the pertinent thermal properties of metal hydrides and other solid state media have also been published [41–45]. An experimental technique for measurement of metal hydride thermal conductivity at various hydrogen pressures has been described by Sun et al. [55] and Suissa et al. [56]. This is particularly important since it is quite difficult to predict the effective thermal conductivity of these materials with existing correlations. Other than metal hydrides, studies have been carried out with carbon based materials as well, like graphite–metal hydride composites [46,47].

Various ways have been proposed in literature to enhance the thermal conductivity of the metal hydride and thus improve the cooling properties of the bed. One of the simplest techniques proposed is to add copper or aluminum balls a few millimeters in diameter to the metal bed [48]. This has the effect of reducing the gravimetric hydrogen storage density, when taking the entire storage bed into consideration because of the addition of materials that do not contribute to hydrogen uptake. Other additives proposed include expanded natural graphite fibers, which when added to the extent of 10% by volume to the metal powder enhances the effective thermal conductivity to about 10 W/mK [33]. Another way of overcoming the problem of low effective thermal conductivity

is to run the hydriding operation by circulating the hydrogen gas through the bed in a loop instead of charging all the hydrogen at once and then carrying out the operation in a batch mode. The effective thermal conductivity of a stagnant gas filled metal hydride bed is far less than that of a bed with a flow of gas through it [110,111]. Though this method may complicate the design of the bed and the associated piping, it is surely a better option than the inclusion of other parasitic materials into the bed and it also is an efficient way of cooling the bed without using any other cooling fluid. Other than adding spheres of copper or aluminum, it has also been proposed to insert solid matrices, wire meshes, metal foams, etc. having high thermal conductivity into the hydride bed and thus improve the effective conductivity [38,48,49,58–61]. Inclusion of metallic plates of copper to divide the bed cross section into a number of sectors is both beneficial for improving the heat transfer as well as ensuring uniform distribution of the powder in the bed and better contact of the gas with the entire amount of solid charged in the vessel. Another method proposed for thermal conductivity enhancement is the use of metal hydride compacts [50–52]. The metal powder is mixed with a powder of aluminum or tin and the mixture is cold pressed to form a compact. In this form the bed thermal conductivity is enhanced significantly and the thermal cycling characteristics are also improved greatly [38]. More recently, the direct synthesis of carbon nanotubes has been proposed for drastic improvement of bed thermal conductivity [53]. It has been estimated that the bed thermal conductivity of about 10 W/mK is attained by this method. A list of effective thermal conductivities for various metal hydride systems has also been provided by Murthy [54].

4. Design of storage beds for hydrogen isotopes

A variety of bed designs to contain the solid state storage material have been proposed by different researchers [62–69]. The fabrication and use of these beds has mainly been in the field of

tritium storage for fusion energy research, so they are based on uranium, ZrCo, ZrFe, etc. alloys. Almost all the tritium handling plants use metal getter beds for short and long term storage of tritium. Thus beds of various designs have been fabricated and their performance has been studied. Some of the general features of these designs are reviewed in the following sections and some general guidelines for the design and/or selection of the beds are provided.

4.1. General considerations

Hydrogen isotope storage beds are generally of the double containment type, particularly when tritium is to be stored in them. This is for lowering permeation losses to the ambient and recovering the permeated hydrogen. The primary storage container is most often a cylindrical vessel, made of SS 316 L. This material, other than possessing high temperature strength is also quite resistant to hydrogen induced embrittlement and is also suitable for welded construction as it is much less susceptible to sensitization reactions. Occasionally oxygen free copper blocks with cylindrical holes bored into them have been used as compartments for accommodating the getter material [112]. Aluminum vessels have been used for tests with low temperature hydrides [67]. Permeation losses through the primary vessel walls can also be minimized through the use of permeation barriers (e.g. oxide layers or coatings on the inner walls) [114].

Both horizontal and vertical bed configurations have been used and studied. The horizontal beds present a larger exposed surface area of the getter material to the gas and they can allow for relatively free thermal expansion during heating. In case of vertical vessels, the powder is generally contained within upper and lower porous disks of sintered steel placed inside the bed, so that the fines of getter material produced in hydriding–dehydriding cycles are mostly confined within the bed and do not contaminate other equipments or instruments of the loop. The typical pore size of these sintered disks or filters is about 2–5 micron. As an alternative to stainless steel sintered disks, ceramic sintered disks can also be used but the maximum allowable temperature for these disks is about 450 °C. Ceramic disks have the risk of cracking under pressure or at high temperatures. In some designs, tubes made of sintered steel have been packed with the getter material and the hydrogen is introduced outside (i.e. on the shell side). This allows for more uniform contact of gas with the getter material and narrow tubes essentially reduce the diffusion path length of the gas through the solid, so that the diffusion related transport resistances to mass transfer are minimized and better heat removal is possible during hydriding. But a horizontal configuration also demands more space requirements (this is a particularly important consideration when the vessel has to be placed inside a glove box) and the bed fabrication (especially a multi-tubular arrangement) is also more difficult. A multi-tubular bed incorporates within itself a double contained arrangement, the packed tube acting as the primary vessel and the shell acting as the secondary containment. For a vertical vessel, the secondary containment is in the form of an outer vessel (like a jacket). Some designs in which the primary vessel is suspended from the top closure or flange of the secondary vessel have been provided [62,112]. This allows for free expansion of the primary vessel when it is heated and reduces thermal stresses that would have otherwise developed if the inner vessel were constrained. The annular space within these vessels is evacuated for preventing conductive and convective heat losses during dehydriding phase. Reduction of radiation heat losses is accomplished by placing stainless steel radiation shields in the annulus. An inert gas like helium, nitrogen or argon can be circulated in the annulus for heat removal during hydriding phase. This gas stream can also be useful for collecting

any hydrogen or tritium that permeates through the walls of the inner vessel and subsequently trapping it in another scavenger bed (if gaseous hydrogen isotope is present) or a moisture trap (if moisture or tritiated moisture is present) [2].

The primary vessel in which the solid is to be held is often divided into sectors through the use of copper segments or strips [65]. This ensures uniform distribution of the solid over the face of the bed which is exposed to hydrogen. This is particularly true for large diameter shallow beds. Narrow diameter tubes will have intrinsically better packing of the solid within them. For shallow beds, to ensure uniform packing, a vibrator arrangement may have to be used or the bed may have to be tapped lightly after solid loading, so that the charged solids are spread uniformly and do not form a heap just below the solid charging port or nozzle.

The beds are generally designed to in such a way that a certain known amount of hydrogen isotope can be introduced into it and it can be allowed to react with the getter material till the pressure drops to the equilibrium pressure at the operating temperature. At this point the reaction stops and there is no more uptake of hydrogen by the getter bed. This is essentially a batch operation. The heat release rate during hydriding is governed by the amount of hydrogen introduced and the kinetics of the hydriding reaction. To enhance heat dissipation during hydriding, a flow-through arrangement in which the hydrogen is recycled through the bed may be used. To limit temperature rise during this phase, the total amount of hydrogen to be stored may be introduced into the bed in smaller batches instead of all at once.

The selection of the length to diameter ratio for the storage bed is governed by factors like the bed configuration (horizontal or vertical), batch operation or recirculation operation and the heat transfer area available at different length to diameter ratios. For batch operations, a shallow bed which presents greater surface area of the solid to the gas and for recirculation mode operations, a narrow configuration which allows for higher superficial velocity through the bed and better heat removal are recommended. The bed height or length should be sufficient to allow heating coils or tapes to be wound properly while the diameter should be sufficient to allow nozzles for gas inlet and outlet ports, ports for thermocouples, etc. to be placed on the top closure. The total external surface area of the bed varies with the length to diameter ratio and the surface temperature of the storage vessel for different configurations should be estimated to arrive at an optimal value for a given application.

For tritium storage, the storage vessel may be provided with the provision for tritium assay using adiabatic calorimetry. This involves utilizing the heat liberated upon radioactive decay of tritium (0.324 W/g m of tritium) to helium-3 to bring about a measurable temperature rise in an inert gas stream (generally helium) passing through the bed. This temperature rise enables one to determine the quantity of tritium in the bed. Thus additional ports on the vessel closure and a gas flow channel through the bed have to be provided for calorimetric determination of tritium content in the bed. This may not be a necessity in case of smaller beds for short term storage of tritium but when large amounts of tritium have to be stored and retrieved later, then it is imperative to accurately estimate the quantity of tritium actually remaining in the bed after a long period of time. Calorimetry is not applicable if it is required to determine the amount of hydrogen or deuterium stored in a bed since they are not radioactive. For estimating the quantity of these isotopes, pressure–volume–temperature based techniques are used.

4.2. Bed heating and cooling arrangements

Heating of the vessel and its contents is required during the dehydriding phase. Most often electrical heating is utilized. Where a secondary vessel has not been provided around the primary

vessel, the heating coil or tape heater may be wound around the outer surface of the vessel. A cartridge heater may also be placed inside the vessel if the vessel diameter is not too large.

Cooling arrangements generally involve passing a gas through the annular space between primary and secondary vessels. In addition the inner vessel may be provided with fins to enhance heat transfer. Tritium containing vessels will have to be handled inside glove boxes, thus the maximum outer surface temperature of the vessel has to be limited to about 60 °C in order to prevent damage of the gloves during handling of the vessel. In case of a single contained vessel, cooling may also be accomplished by providing brazed cooling coils over the outer surface of the vessel through which cooling fluid (generally an inert gas or water) may be circulated. For double contained vessels, brazed cooling coils have been used but the design becomes slightly more complicated and more penetrations are required on the top flange or vessel closure to accommodate the coolant inlet and outlet connections.

A more elaborate design involving a coiled tube heat exchanger integrated with the bed has been proposed by Visaria and Mudawar [67]. The bed has been fabricated for withstanding pressure up to 280 bar. The coil occupies only about 7% of the bed volume but it has reportedly increased the hydriding rate by 75%. The coil has been so designed to provide adequate contact of nearly all the solid with the coolant during hydriding phase. The storage material in this case was Ti_{1.1}CrMn and the material of construction was aluminum.

5. Kinetic models of hydriding and dehydriding reactions

The importance of studying the kinetics of hydriding and dehydriding processes cannot be overemphasized. It is directly related to the time it will take a given material to adsorb hydrogen at a given pressure and temperature or to recover hydrogen from a bed. For storage applications in the hydrogen based automobile industry, the time of filling and discharge of hydrogen from a solid bed is of utmost importance, so it is for the fusion energy sector where tritium and deuterium will have to be supplied to the plasma at required rates on demand. Therefore the kinetics of hydrogen uptake and desorption have been studied extensively for many metals and alloy systems under various conditions of temperature and pressure [70–104]. The kinetic behavior exhibited by these systems is quite different, depending on the materials. Moreover the hydrogen pressure and temperature range studied are all quite different, leading to differences in kinetics observed. For the fusion energy field, the kinetics of hydriding and dehydriding of the relatively simpler heavy metal and metal alloy systems (U, ZrCo, ZrFe₂, etc.) are much more relevant while a larger variety of alloys and complex hydrides are potential candidates for the automobile industry.

The hydriding or dehydriding reaction is mostly visualized as a typical gas-solid, non-catalytic reaction comprising the usual steps of adsorption, penetration through surface, internal diffusion and chemical reaction [71]. The method of analysis used is usually similar to the shrinking core model or modified versions of it. The rate determining step is usually reported to be the internal diffusion step or the growth and nucleation of the hydride phase (β phase). Generally the rate equations have been so formulated so as to have some kind of power law dependence on gas concentration [105]. But when thermogravimetric techniques have been utilized to follow the kinetics, the rate equation is generally formulated in terms of the weight fraction of metal hydrided or dehydrided. For many of the kinetic studies exhibited above, kinetic parameters (i.e. rate constants and activation energy values) have been reported. The rate constant value is expected to differ even for the same material examined under similar conditions and this difference may be attributed to the

difference in the way of preparation of the base metal or alloy and its state of activation. Moreover the bed design also has a significant role to play in controlling the overall reaction characteristics. In many cases involving magnesium, the use of other metal doping agents (e.g. Zr, V, Ni, etc.) have been shown to improve the hydriding kinetics. The use of metals or their alloys in the form of nanoparticles has also been shown to improve the hydriding kinetics [96] but this may not always be a feasible way of enhancing hydrogen adsorption or desorption rates because the technology for the large scale production and quality control of nanoparticles is yet to be developed, thus this technique is expensive and hard to implement widely as of now. Further most of the alloys and metals that react with hydrogen also react with moisture or oxygen, sometimes with explosive violence. The chemical reactivity and pyrophority hazards are also greatly enhanced when these materials have to be handled in nanoparticle forms. The study of hydrogen adsorption on uranium is especially relevant to the field of fusion research, thus there are several works devoted to the study of kinetics of hydriding and dehydriding of uranium [105–108]. Similarly ZrCo and its hydriding and dehydriding kinetics have been investigated by a number of investigators [17,18,68,69].

It is advisable to study the kinetics of the particular material being considered for a given application before further design calculations are done. Since the sizing of a storage bed is often done based on stoichiometric uptake of hydrogen by the solid, the kinetics is not very relevant but to determine rates of heat removal and supply, it is necessary to know the kinetics. In the absence of facilities to study or determine the kinetics, conservative estimates are necessary based on literature data for similar systems. It has been reported that most hydriding reactions are essentially completed within a few minutes, provided the material is well activated and is in the form of a free flowing powder [109], so along with the enthalpy of reaction for the given material, this can provide some estimation of the heat generation rate during hydriding and therefore the heat removal capability required during the hydriding process so that nearly isothermal conditions can be achieved.

6. Technological difficulties in solid state hydrogen storage

The solid state immobilization and storage of hydrogen is certainly an attractive option particularly when safety and compactness of the storage system are of prime concern. The successful implementation of hydrogen based automobile systems requires that the storage issues be addressed first. The principal challenge to be overcome before hydrogen can be extensively stored as a solid hydride is the development of an appropriate material that has all (or nearly all) the desirable qualities for the particular application. Once a material is shortlisted, the technology of synthesizing that material on a large scale has to be developed. The design of a suitable container for the storage bed, selection of appropriate materials of construction and fabrication technologies and associated heating and cooling systems for it can be further improved before one particular design is standardized, for stationary storage applications or for fusion energy programs. Some other technological issues that have to be taken care of after a material is selected are briefly mentioned below [57,115]:

- i). All the materials for hydrogen storage examined so far need an initial activation step that involves evacuating the container having the storage matrix in it at high temperatures, followed by exposure to hydrogen at high pressure. The material must thus be hydrided and dehydrided several times till a free flowing activated powder is obtained that readily adsorbs hydrogen. The difficulty is that the highly active powder not only adsorbs hydrogen but also reacts with gases like oxygen, nitrogen and its oxides, moisture, etc. These side reactions reduce the adsorptive capacity of the metal for hydrogen. It has been suggested that

- the surface of the solid matrix be protected by techniques such as fluorination i.e. pre-treatment with potassium fluoride/hydrofluoric acid solution that increases the surface area of the matrix and allows it to be most selective to reactions with hydrogen [116].
- ii). The volume expansion of the solid matrix on hydriding and its subsequent break-up into fine powder changes the packing characteristics of the bed affects its heat transfer behavior by altering the effective thermal conductivity of the matrix and induces large mechanical stresses on the bed walls. Horizontally oriented beds are better for dealing with the problems of induced mechanical stresses. Also sufficient void volume has to be provided in the bed to take care of volume expansion on hydriding.
 - iii). After several hydriding-dehydriding cycles, the alloy based materials often suffer disproportionation reactions, segregation into different elements instead of remaining as the alloy and disintegration. All these cause a loss of adsorptive capacity.
 - iv). True equilibrium conditions are very often not attained during hydriding and dehydriding steps. The actual pressure temperature-composition behavior of any material depends greatly on the engineering design of the system and this reduces the amount of hydrogen that can actually be recovered.
 - v). Low cost materials and material synthesis techniques need to be developed. Additionally, low temperature, low pressure materials should also be developed since for high pressure materials, the container vessel wall thickness increases greatly heavy and lowers the thermal efficiency of the process since a large amount of thermal energy has to be provided to just heat the vessel during the dehydriding step.

7. Computational models of solid state hydrogen storage beds

A significant amount of effort has been directed to the mathematical modeling and simulation of the performance of the hydrogen storage beds [117–124], especially containers using the concept of reversible hydrides for hydrogen storage. Both commercially available computational packages (like COMSOL™ and FLUENT™) as well as in house codes have been used for these studies. The principal aims for these studies have been to obtain composition and temperature profiles for the beds as functions of time and position (radial and/or axial) on the bed. Simulations as well as experimental studies have also been performed to study the stress-strain distributions in the bed [125].

For the simulation studies the bed is generally visualized as having two sections (and hence two computational zones or domains) – one being the porous metal/metal hydride (i.e. the porous solid part) and the other being hydrogen gas only (i.e. the additional expansion volume filled with hydrogen). The typical assumptions made to arrive at a mathematical model of the storage bed are the following [119,121,124]:

- i). The gaseous zone and the porous solid zone are in thermal equilibrium (i.e. the same temperature variable is used for both).
- ii). The porous solid is isotropic and uniform (i.e. thermal conductivity, density, specific heat, porosity are the same in radial and axial directions).
- iii). The gas is an ideal gas.
- iv). Solid thermal properties do not change significantly with the extent of hydriding.
- v). The equilibrium pressure versus temperature relationship can be related through the Van't Hoff law and the kinetics of hydriding and dehydriding can be expressed through Arrhenius-type rate

laws. The values of these constants are specific to the particular metal or alloy storage medium and the particular hydrogen isotope being considered.

- vi). The velocity of the gas in the porous region can be expressed through Darcy's law.
- vii). The heat loss to the ambient or to a cooling fluid circulating outside the bed can be incorporated in the wall boundary condition by the use of an overall heat transfer coefficient, if it is assumed that the coolant temperature remains almost constant. Otherwise a separate energy balance equation has to be written for the coolant.

The typical governing equations used for numerical simulation of the temperature and composition profiles in the bed are shown in Eqs. (1)–(13) [119,121,124].

Material balance for hydrogen:

$$\epsilon \frac{\partial \rho_g}{\partial t} + \nabla \cdot (\rho_g v_g) = -\dot{m} \quad (1)$$

Material balance for the solid:

$$\frac{dm_s}{dt} = V_s \dot{m} \quad (2)$$

Energy balance for the gas:

$$\epsilon \frac{\partial (\rho_g C_{pg} T_g)}{\partial t} = -\nabla \cdot (k_g \nabla T_g) + h_{sg} A_h (T_s - T_g) - v_g \nabla (\rho_g C_{pg} T_g) - \dot{m} C_{pg} T_g \quad (3)$$

Energy balance for the solid:

$$(1 - \epsilon) \rho_s C_{ps} \frac{\partial (T_s)}{\partial t} = -(k_s \nabla^2 T_s) - h_{sg} A_h (T_s - T_g) - \dot{m} (\Delta H - C_{ps} T_s) \quad (4)$$

If the gas and solid temperature are taken as the same based on assumption (i) mentioned above, the single energy balance equation is written as

$$(\rho C_p)_e \frac{\partial T}{\partial t} + (\rho_g C_{pg}) (v_g \cdot \nabla T) = \nabla \cdot (k_e \nabla T) + \dot{m} \Delta H \quad (5)$$

Rate equation for hydriding step:

$$\dot{m} = k_a \exp\left(\frac{-E_a}{RT_s}\right) \ln\left(\frac{P}{P_{eq}}\right) (c_{ss} - c(t)) \quad (6)$$

Rate equation for dehydriding:

$$\dot{m} = k_d \exp\left(\frac{-E_d}{RT_s}\right) \left(\frac{P - P_{eq}}{P_{eq}}\right) c_{ss} \quad (7)$$

Effective thermal conductivity:

$$k_e = \epsilon k_g + (1 - \epsilon) k_s \quad (8)$$

Effective specific heat capacity:

$$(\rho C_p)_e = \epsilon (\rho_g C_{pg}) + (1 - \epsilon) (\rho_s C_{ps}) \quad (9)$$

Darcy's law:

$$v_g = -\frac{K}{\mu} \nabla P \quad (10)$$

Kozeny–Carman equation:

$$K = \frac{d_p^2 \epsilon^3}{150(1 - \epsilon)^2} \quad (11)$$

Gas density from ideal gas law:

$$\rho_g = \frac{M_g P}{RT} \quad (12)$$

Van't Hoff's law:

$$\ln(P_{eq}) = A - (B/T) \quad (13)$$

The numerical integration of all these coupled equations along with appropriate boundary conditions and initial conditions enables one to determine the temperature and concentration distribution in the bed. Boundary and initial conditions differ from case to case (depending on geometry of the system) and thus they have no generalized forms and so are not presented here.

8. Summary and conclusions

Solid state hydrogen storage systems have been studied widely, especially from the materials point of view. There is a great variety of materials that have attracted attention because of their unique advantages with respect to hydrogen storage but they also present practical difficulties with respect to the conditions for hydriding and dehydriding and the maximum storage capacity achievable from them. Materials like uranium, titanium and some binary alloys of Zr, Co, Ti, etc. have been used in the nuclear industry for tritium storage. Other materials like carbon nanotubes, zeolites and MOFs have also been studied in this context. The benefits and difficulties associated with each class of material have been pointed out in this paper. All in all, metal and metal alloy based systems appear to hold the most promise for solid state hydrogen storage for both mobile and stationary applications.

Apart from providing an overview of the material options available to users, this article focuses on the engineering aspects of designing a practical solid state hydrogen storage system using metallic getter materials. This activity requires the knowledge of thermodynamic, transport and kinetic behavior of the chosen metal–hydrogen system. Such information has been reported extensively in literature and an enormous and steadily increasing body of information has been built up. These data are important for the engineering design of any hydrogen storage system. At the heart of such a system lies a pressure vessel that has to be designed while keeping in mind the process requirements and necessary safety features. Compactness, proper heat supply and removal arrangements and built in safety features have to be considered while designing the vessel. Various such designs have been proposed, each having their own advantages and disadvantages. The most important issue in the design of such a system pertains to effective heat supply and removal for the recovery and the hydriding phases respectively, for which various design concepts have been implemented. This review presents several important concepts for efficient bed design and engineering of the storage system. Other than the vessel design, several technological challenges, arising from low storage capacity, loss of capacity after certain number of cycles, poisoning of the getter material, that have to be overcome before solid state storage of hydrogen isotopes becomes a widely used process. Despite the large number of materials studied so far, no one material has yet been found to be suitable in all respects for hydrogen storage thus providing the impetus necessary for further research activities in

this field. This review thus introduces a reader to the various aspects of this field, right from materials research, to the actual engineering and design of the system, as well as its mathematical modeling.

References

- [1] Rand DAJ, Dell RM. Hydrogen energy-challenges and prospects. 1st ed. Cambridge: RSC Publishing; 2008; 1–20.
- [2] Shmaya WT. Tritium processing using scavenger beds: theory and operation. In: Mannone F, editor. Safety in tritium handling technology. Ispra, Italy: Kluwert Academic Publishers; 1993. p. 107–30.
- [3] Durbin DJ, Malarquier-Jugroot C. Review of hydrogen storage techniques for on board vehicle applications. Int J Hydrol Energy 2013;38:14595–617.
- [4] Gill JT, Anderson BE, Watkins RA, Pierce CW. Tritium storage/delivery and associated cleanup systems for TFR. J Vac Sci Technol A 1983;1(2):856–63.
- [5] Schira P, Hutter G, Jourdan G, Penzhorn R-D. The tritium laboratory Karlsruhe: laboratory design and equipment. Fusion Eng Des 1991;18:19–26.
- [6] Mitrokhin SV, Bezuglaya TN, Verbetsky VN. Structure and hydrogen sorption properties of (Ti,Zr)–Mn–V alloys. J Alloy Compd 2002;330–332:146–51.
- [7] Liu B-H. Hydrogen-metal systems: hydride forming alloys (properties and characteristics, database information). In: Martin JW, editor. Concise encyclopedia of materials for energy systems. Oxford, UK: Elsevier Limited; 2009. p. 243–59.
- [8] Sivakumar R, Ramaprabhu S, Rama Rao KVS, Bodo Mayer, Schmidt PC. Hydrogen absorption-desorption characteristics, kinetics of hydrogen absorption and thermodynamics of dissolved hydrogen in $Zr_{0.1}Tb_{0.9}Fe_{1.5}Co_{1.5}$. J Alloy Compd 2000;302:146–54.
- [9] Clark NJ, Wu E. Hydrogen absorption in the Zr–Al system. J Alloy Compd 1990;163:227–43.
- [10] Broom DP. Hydrogen storage materials. 1st ed. London: Springer-Verlag Limited; 2011; 19–59.
- [11] Penzhorn R-D. Tritium storage. In: Mannone F, editor. Safety in tritium handling technology. Ispra, Italy: Kluwert Academic Publishers; 1993. p. 107–30.
- [12] Miedema AR, Buschow KHJ, Van Mal HH. Which intermetallic compounds of transition elements form stable hydrides? J Less Common Met 1976;49:463–72.
- [13] Huston EL, Sandrock GD. Engineering properties of metal hydrides. J Less Common Met 1980;49:435–43.
- [14] Bogdanovic B, Sandrock G. Catalyzed complex metal hydrides. MRS Bull 2002;27(9):712–6.
- [15] Selvam PK, Muthukumar P, Linder M, Mertz R, Kulenovic R. Measurement of thermochemical properties of some metal hydrides-Titanium (Ti), misch metal (Mm) and lanthanum (La) based alloys. Int J Hydrol Energy 2013;38:5288–301.
- [16] Sandrock G. A panoramic overview of hydrogen storage alloys from a gas reaction point of view. J Less Common Met 1999;293–295:877–88.
- [17] Shmaya WT, Heics AG, Kherani NP. Comparison of uranium and zirconium cobalt for tritium storage. J Less Common Met 1990;162:117–27.
- [18] Penzhorn R-D, Devilliers M, Sirch M. Evaluation of ZrCo and other getters for tritium handling and storage. J Nucl Mater 1990;170:217–31.
- [19] Peacock HB. Pyrophority of uranium. WSRTR-92-106 1992 (DOE technical report) Available from: <http://www.osti.gov/scitech/servlets/purl/10155050> [accessed 19.09.13].
- [20] Heung LK. Titanium for long term tritium storage. WSRTR-94-0596 (DOE technical report) Available from: <http://www.osti.gov/bridge/servlets/purl/10117162vpKxNH/webviewable/10117162.pdf> [accessed 19.09.13].
- [21] Ionete EI, Monea B, Zamfirache M. Hydrogen and deuterium sorption on titanium under vacuum conditions. In: Mladenov V, Stork M, Choras R, editors. Proceedings of the 2nd international conference on circuits, systems, control, signals (CSCS '11), Prague: WSEAS Press; 2011. p. 156–8.
- [22] Dillon AC, Jones KM, Bekkedahl TA, Kiang CH, Bethune DS, Heben MJ. Storage of hydrogen in single-walled carbon nanotubes. Nature 1997;386:377–9.
- [23] Cheng H, Yang Q, Liu C. Hydrogen storage in carbon nanotubes. Carbon 2001;39:1447–54.
- [24] Hirscher M, et al. Are carbon nanostructures an efficient hydrogen storage medium? J Alloy Compd 2003;356–357:433–7.
- [25] Klebanoff L, Keller J. Final report for the DOE metal hydride centre of excellence. SAND2012-0786 (SANDIA report) Available from: http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/metal_hydride_coe_final_report.pdf [accessed 19.09.13].
- [26] Umegaki T, Yan J, Zhang X, Shioyama H, Kuriyama N, Xu Q. Boron- and nitrogen-based chemical hydrogen storage materials. Int J Hydrol Energy 2009;34:2303–11.
- [27] Siegel DJ, Wolverton C, Ozoliņš V. Thermodynamic guidelines for the prediction of hydrogen storage reactions and their application to destabilized hydride mixtures. Phys Rev B 2007;76 (134102-1–134102-6).
- [28] Sakintuna B, Darkrim-Lamari F, Herscher M. Metal hydride materials for solid hydrogen storage: a review. Int J Hydrol Energy 2007;32:1121–40.
- [29] Bogdanovic B, Schwickardi M. Ti-doped alkali metal aluminium hydrides as potential novel reversible hydrogen storage materials. J Alloy Compd 1997;253–254:1–9.

- [30] Rosi NL, et al. Hydrogen storage in microporous metal-organic frameworks. *Science* 2003;300:1127.
- [31] Hirscher M, Panella B, Schmitz B. Metal-organic frameworks for hydrogen storage. *Microporous Mesoporous Mater* 2010;129:335–9.
- [32] Murray LJ, Dinca M, Long JR. Hydrogen storage in metal-organic frameworks. *Chem Soc Rev* 2009;38:1294–314.
- [33] Dedrich RE. Solid-state hydrogen storage system design. In: Walker G, editor. *Solid-state hydrogen storage: materials and chemistry*. Cambridge, UK: Woodhead Publishing Limited; 2008. p. 82–103.
- [34] Pant KK, Gupta RB. Hydrogen storage in carbon materials. In: Gupta RB, editor. *Hydrogen fuel: production, transport and storage*. Boca Raton, Florida, USA: CRC Press, Taylor and Francis Group; 2009. p. 381–436.
- [35] Bogdanovic B, Brand RA, Marjanovic A, Schwickardi M, Tölle J. Metal-doped sodium aluminum hydrides as potential new hydrogen storage materials. *J Alloy Compd* 2000;302(1–2):36–58.
- [36] Jensen CM, Zidan R, Mariels N, Hee A, Hagen C. Advanced titanium doping of sodium aluminum hydride: segue to a practical hydrogen storage material? *Int J Hydrot Energy* 1999;24(5):461–5.
- [37] Dalebrook AF, Gan W, Grasemann M, Moret S, Laurenczy G. Hydrogen storage: beyond conventional methods. *Chem Commun* 2013;49:8735–51.
- [38] Yang FS, Wang GX, Zhang ZX, Meng XY, Rudolph V. Design of the metal hydride reactors – a review on the key technical issues. *Int J Hydrot Energy* 2010;35(3832):3840.
- [39] Antwerpen W van, Toit CG du, Rousseau PG. A review of correlations to model the packing structure and effective thermal conductivity in packed beds of mono-sized spherical particles. *Nucl Eng Des* 2010;240:1803–18.
- [40] Kandula M. On the effective thermal conductivity of porous packed beds with uniform spherical particles. *J Porous Media* 2011;14(10):919–26.
- [41] Hahne E, Kallweit J. Thermal conductivity of metal hydride materials for storage of hydrogen: experimental investigation. *Int J Hydrot Energy* 1998;23(2):107–14.
- [42] Ghafir MFA, Batcha MFM, Raghavan VR. Prediction of the thermal conductivity of metal hydrides: the inverse problem. *Int J Hydrot Energy* 2009;34:7125–30.
- [43] Suda S, Kobayashi N, Yoshida K. Thermal conductivity in metal hydride beds. *Int J Hydrot Energy* 1981;6(5):521–8.
- [44] Sun D-W, Deng S-J. A theoretical model predicting the effective thermal conductivity in powdered metal hydride beds. *Int J Hydrot Energy* 1990;15(5):331–6.
- [45] Flueckiger S, Voskuilen T, Pourpoint T, Fisher ST, Zheng Y. In situ characterization of metal hydride thermal transport properties. *Int J Hydrot Energy* 2010;35(2):614–21.
- [46] Pohlmann C, Röntzsich L, Weißgärtner T, Kieback B. Heat and gas transport properties in pelletized hydride-graphite-composites for hydrogen storage applications. *Int J Hydrot Energy* 2013;38(3):1685–91.
- [47] Pohlmann C, Röntzsich L, Kalinichenko S, Hutsch T, Kieback B. Magnesium alloy-graphite composites with tailored heat conduction properties for hydrogen storage applications. *Int J Hydrot Energy* 2010;35(23):12829–36.
- [48] Suda S, Komazaki Y, Kobayashi N. Effective thermal conductivity of metal hydride beds. *J Less-Common Met* 1983;89:317–24.
- [49] Nagel M, Komazaki Y, Suda S. Effective thermal conductivity of a metal hydride bed augmented with a copper wire matrix. *J Less-Common Met* 1986;120:35–43.
- [50] Ron M, Gruen D, Mendelsohn M, Sheet I. Preparation and properties of porous metal hydride compacts. *J Less-Common Met* 1980;74(2):445–8.
- [51] Bershadsky E, Josephy Y, Ron M. Permeability and thermal conductivity of porous metallic matrix hydride compacts. *J Less-Common Met* 1989;153:65–78.
- [52] Ron M, Bershadsky E, Josephy Y. The thermal conductivity of porous metal matrix hydride compacts. *J Less-Common Met* 1991;172–174:1138–46.
- [53] Inoue S, Iba Y, Matsumura Y. Drastic enhancement of effective thermal conductivity of a metal hydride packed bed by direct synthesis of single-walled carbon nanotubes. *Int J Hydrot Energy* 2012;37:1836–41.
- [54] Murthy SS. Heat and mass transfer in solid state hydrogen storage: a review. *J Heat Transf* 2012;134 (031020-1–031020-11).
- [55] Sun D, Deng S. Theoretical descriptions and experimental measurements on the effective thermal conductivity in metal hydride powder beds. *J Less-Common Met* 1990;160:387–95.
- [56] Suissa E, Jacob I, Hadari Z. Experimental measurements and general conclusions on the effective thermal conductivity of powdered metal hydrides. *J Less-Common Met* 1984;104:287–95.
- [57] Zhang J, Fisher TS, Ramachandran PV, Gore JP, Mudawar I. A review of heat transfer issues in hydrogen storage technologies. *J Heat Transf* 2005;127:1391–9.
- [58] Schmierer EN, Razani A. Self-consistent open-celled metal foam model for thermal applications. *J Heat Transf* 2006;128(11):1194–203.
- [59] Mellouli S, Dhaou H, Askri F, Jemni A, Ben Nasrallah S. Hydrogen storage in metal hydride tanks equipped with metal foam heat exchanger. *Int J Hydrot Energy* 2009;34(23):9393–401.
- [60] Tsai ML, Yang TS. On the selection of metal foam volume fraction for hydriding time minimization of metal hydride reactors. *Int J Hydrot Energy* 2010;35(20):11052–63.
- [61] Laurencelle F, Goyette J. Simulation of heat transfer in a metal hydride reactor with aluminum foam. *Int J Hydrot Energy* 2007;32(14):2957–64.
- [62] Konishi S, Nagasaki T, Yokokawa N, Naruse Y. Development of zirconium cobalt beds for recovery, storage and supply of tritium. *Fusion Eng Des* 1989;10:355–8.
- [63] Hayashi T, Suzuki T, Yamada M, Shu W, Yamanishi T. Safe handling experience of a tritium storage bed. *Fusion Eng Des* 2008;83:1429–32.
- [64] Shmyday WT, Mayer P. Uranium beds for temporary tritium storage. *J Less-Common Met* 1984;104:239–50.
- [65] Singleton MF, Alire RM. Traps for scavenging hydrogen isotopes. 3rd Topical meeting on the technology of controlled nuclear fusion, Santa Fe, NM, May 9–11, 1978.
- [66] Nishikawa M, Kido H, Kotoh K, Sugisaki M. Titanium sponge bed to scavenge tritium from inert gases. *J Nucl Mater* 1983;115:101–9.
- [67] Visaria M, Mudawar I. Coiled-tube heat exchanger for high-pressure metal hydride hydrogen storage systems-Part 1. Experimental study. *Int J Heat Mass Transf* 2012;55:1782–9.
- [68] Chung D, et al. Fusion fuel gas recovery and delivery characteristics on a tray-type ZrCo bed. *Fusion Eng Des* 2011;86:2233–6.
- [69] Shim M, et al. Heat analysis on the initial reference design of ZrCo hydride beds for ITER. *Fusion Eng Des* 2008;83:1433–7.
- [70] Bloch J, Mintz M. Kinetics and mechanisms of metal hydrides formation – a review. *J Alloy Compd* 1997;253–254:529–41.
- [71] Muthukumar P, Satheesh A, Linder M, Mertz R, Groll M. Studies on hydriding kinetics of some La-based metal hydride alloys. *Int J Hydrot Energy* 2009;34(17):7253–62.
- [72] Chernov I, Bloch J, Voit A, Gabis I. Influence of metal powder particle's shape on the kinetics of hydriding. *Int J Hydrot Energy* 2010;35(1):253–8.
- [73] Simonović BR, Mentus S, Šušić MV. Kinetics of tantalum hydriding: the effect of palladination. *Int J Hydrot Energy* 2000;25(11):1069–73.
- [74] Fan X, Xiao X, Chen L, Han L, Li S, Ge H, Wang Q. Hydriding-dehydriding kinetics and the microstructure of La- and Sm-doped NaAl₄ prepared via direct synthesis method. *Int J Hydrot Energy* 2011;36(17):10861–9.
- [75] Liu X, Zhu Y, Li L. Hydriding characteristics of prepared by mechanical milling of the product of hydriding combustion synthesis. *Int J Hydrot Energy* 2007;32(13):2450–4.
- [76] Wang XL, Suda S. Kinetics of the hydriding-dehydriding reactions of the hydrogen–metal hydride systems. *Int J Hydrot Energy* 1992;17(2):139–47.
- [77] Xiao X, Chen L, Wang X, Li S, Wang Q, Chen C. Influence of temperature and hydrogen pressure on the hydriding/dehydriding behavior of Ti-doped sodium aluminum hydride. *Int J Hydrot Energy* 2007;32(16):3954–8.
- [78] Simonovic BR, Mentus S, Dimitrijevic R, Šusic MV. Multiple hydriding/dehydriding of Zr_{1.02}Ni_{0.98} alloy. *Int J Hydrot Energy* 1999;24(5):449–54.
- [79] Bambhaniya KG, Grewal GS, Shrinet V, Singh NL, Govindan TP. Fast hydriding Mg–Zr–Mn–Ni alloy compositions for high capacity hydrogen storage application. *Int J Hydrot Energy* 2012;37(4):3671–6.
- [80] Pan YB, Wu Y, Li Q. Modeling and analyzing the hydriding kinetics of Mg–LaNi₅ composites by Chou model. *Int J Hydrot Energy* 2011;36(20):12892–901.
- [81] Ngameni R, Mbemba N, Grigoriev SA, Millet P. Comparative analysis of the hydriding kinetics of LaNi₅, La_{0.8}Nd_{0.2}Ni₅ and La_{0.7}Ce_{0.3}Ni₅ compounds. *Int J Hydrot Energy* 2011;36(6):4178–84.
- [82] Chung HS, Lee JY. Effect of partial substitution of Mn and Ni for Fe in FeTi on hydriding kinetics. *Int J Hydrot Energy* 1986;11(5):335–9.
- [83] Wang CS, Wang XH, Lei YQ, Chen CP, Wang QD. The hydriding kinetics of MINi₅-I. Development of the model. *Int J Hydrot Energy* 1996;21(6):471–8.
- [84] Khrusanova M, Terzieva M, Peshev P. On the hydriding kinetics of the alloys La₂Mg₁₇ and La_{2-x}Ca_xMg₁₇. *Int J Hydrot Energy* 1986;11(5):331–4.
- [85] Han JI, Lee JY. Hydriding kinetics of LaNi₅ and LaNi_{4.7}Al_{0.3}. *Int J Hydrot Energy* 1989;14(3):181–6.
- [86] Song MY, Lee JY. A study of the hydriding kinetics of Mg-(10–20w/o)LaNi₅. *Int J Hydrot Energy* 1983;8(5):363–7.
- [87] Luo Q, An X, Pan Y, Zhang X, Zhang J, Li Qian. The hydriding kinetics of Mg–Ni based hydrogen storage alloys: a comparative study on Chou model and Jander model. *Int J Hydrot Energy* 2010;35(15):7842–9.
- [88] Ming L, Lavendar E, Goudy AJ. The hydriding and dehydriding kinetics of some RCo₅ alloys. *Int J Hydrot Energy* 1997;22(1):63–6.
- [89] Han JS, Lee JY. A study of the hydriding kinetics of Mg₂Ni at the near isothermal condition. *Int J Hydrot Energy* 1987;12(6):417–24.
- [90] Song MY, Ahn HJ, Park HR. A study of the hydriding and dehydriding kinetics of a mixture of 2 Mg and Co. *Int J Hydrot Energy* 1991;16(3):223–9.
- [91] Dhaou H, Askri F, Ben Salah M, Jemni A, Nasrallah B, Lamloumi J. Measurement and modelling of kinetics of hydrogen sorption by LaNi₅ and two related pseudobinary compounds. *Int J Hydrot Energy* 2007;32(5):576–87.
- [92] Wang XH, Wang CS, Chen CP, Lei YQ, Wang QD. The hydriding kinetics of MINi₅-II. Experimental results. *Int J Hydrot Energy* 1996;21(6):479–84.
- [93] Mattsoff S, Noréus D. Hydriding kinetics of Mg₂Ni at low temperatures where intrinsic processes dominate the reaction rates. *Int J Hydrot Energy* 1987;12(5):333–5.
- [94] Stucki F. Hydriding and dehydriding kinetics of Mg₂Ni above and below the structural phase transition. *Int J Hydrot Energy* 1983;8(1):49–51.
- [95] Chernov I, Bloch J, Gabis I. Mathematical modelling of UH₃ formation. *Int J Hydrot Energy* 2008;33(20):5589–95.
- [96] Lebouin C, Soldo Y, Grigoriev SA, Guymont M, Millet P. Kinetics of hydrogen sorption by palladium nanoparticles. *Int J Hydrot Energy* 2013;38(2):966–72.

- [97] Chi H, Chen C, Chen L, An Y, Wang Q. Hydriding/dehydriding properties of $\text{La}_2\text{Mg}_{16}\text{Ni}$ alloy prepared by mechanical ball milling in benzene and under argon. *Int J Hydrog Energy* 2004;29(7):737–41.
- [98] Li Q, Chou K, Lin Q, Jiang L, Zhan F. Hydrogen absorption and desorption kinetics of Ag–Mg–Ni alloys. *Int J Hydrog Energy* 2004;29(8):843–9.
- [99] Domschke T, Schütt E, Haas I. Research on kinetics of hydrogen sorption in low-temperature metal hydrides. *Int J Hydrog Energy* 1989;14(9):671–6.
- [100] Mazzolai G. Kinetics of hydrogen absorption by scandium at high temperature. *Int J Hydrog Energy* 2011;36(7):4507–12.
- [101] Wu CZ, Yao XD, Zhang H. Hydriding/dehydriding properties of $\text{MgH}_2/5\text{ wt\% Ni}$ coated CNFs composite. *Int J Hydrog Energy* 2010;35(1):247–52.
- [102] Chung HS, Lee J. Hydriding and dehydriding reaction rate of FeTi intermetallic compound. *Int J Hydrog Energy* 1985;10(7–8):537–42.
- [103] Song MY, Kwon SN, Park HR, Bobet J. Improvement of hydriding and dehydriding rates of Mg via addition of transition elements Ni, Fe, and Ti. *Int J Hydrog Energy* 2011;36(20):12932–8.
- [104] Liu J, Zhang X, Li Q, Chou K, Xu K. Investigation on kinetics mechanism of hydrogen absorption in the $\text{La}_2\text{Mg}_{17}$ -based composites. *Int J Hydrog Energy* 2009;34(4):1951–7.
- [105] Stakebake JL. Kinetics for the reaction of hydrogen with uranium powder. *J Electrochem Soc* 1979;126(9):1596–601.
- [106] Bloch J. The hydriding kinetics of activated uranium powder under low (near equilibrium) hydrogen pressure. *J Alloy Compd* 2003;361:130–7.
- [107] Balooch M, Hamza AV. Hydrogen and water vapor adsorption on and reaction with uranium. *J Nucl Mater* 1996;230:259–70.
- [108] Bloch J, Mintz MH. Kinetics and mechanism of the U–H reaction. *J Less-Common Met* 1981;81:301–20.
- [109] Suda S, Kobayashi N, Yoshida K. Reaction kinetics of metal hydrides and their mixtures. *J Less-Common Met* 1980;73:119–26.
- [110] Wen D, Ding Y. Heat transfer of gas flow through a packed bed. *Chem Eng Sci* 2006;61:3532–42.
- [111] Aachenbach E. Heat and flow characteristics of packed beds. *Exp Therm Fluid Sci* 1995;10:17–27.
- [112] Cullingford HS, Wheeler MG, McMullen JW. A hydride storage bed design for tritium systems test assembly. (DOE technical report server) LA-UR-81-1906; 2009 Available from: <http://www.osti.gov/scitech/biblio/46456> [accessed 11.11.13].
- [113] Chauk SS, Fan LS. Heat transfer in packed and fluidized beds. In: Rohsenow WM, Hartnett JP, Cho Yi, editors. *Handbook of heat transfer*. 3rd ed. New York, USA: McGraw Hill Publishers; 1998. p. 13.1–14.
- [114] Henager Jr CH. Hydrogen permeation barrier coatings. In: Jones RH, Thomas CJ, editors. *Materials for the hydrogen economy*. Boca Raton, USA: CRC Press, Taylor and Francis Group; 2008. p. 181–90.
- [115] Suda S. Hydrogen-metal systems: technological and engineering aspects. In: Martin JW, editor. *Concise encyclopedia of materials for energy systems*. Oxford, UK: Elsevier Limited; 2009. p. 260–6.
- [116] Li ZP. Hydrogen–metal systems: fluorinated metal hydrides. In: Martin JW, editor. *Concise encyclopedia of materials for energy systems*. Oxford, UK: Elsevier Limited; 2009. p. 230–42.
- [117] Chung CA, Ho C. Thermal–fluid behavior of the hydriding and dehydriding processes in a metal hydride hydrogen storage canister. *Int J Hydrog Energy* 2009;34:4351–64.
- [118] Visaria M, Mudawar I. Experimental investigation and theoretical modeling of dehydriding process in high-pressure metal hydride hydrogen storage systems. *Int J Hydrog Energy* 2012;37:5735–49.
- [119] Askri F, Jemni A, Nasrallah SB. Prediction of transient heat and mass transfer in a closed metal–hydrogen reactor. *Int J Hydrog Energy* 2004;29:195–208.
- [120] Muthukumar P, Singhal A, Bansal GK. Thermal modeling and performance analysis of industrial-scale metal hydride based hydrogen storage container. *Int J Hydrog Energy* 2012;37 (14531–14364).
- [121] Freni A, Cipiti F, Cacciola G. Finite element-based simulation of a metal hydride-based hydrogen storage tank. *Int J Hydrog Energy* 2009;34:8574–82.
- [122] Askri F, Jemni A, Nasrallah SB. Study of two-dimensional and dynamic heat and mass transfer in a metal–hydrogen reactor. *Int J Hydrog Energy* 2003;28:537–57.
- [123] Johnson TA, Kanouff MP, Dedrick DE, Evans GH, Jorgensen HW. Model-based design of an automotive-scale, metal hydride hydrogen storage system. *Int J Hydrog Energy* 2012;37:2835–49.
- [124] Ye J, Jiang L, Li Z, Liu X, Wang S, Li X. Numerical analysis of heat and mass transfer during absorption of hydrogen in metal hydride based hydrogen storage tanks. *Int J Hydrog Energy* 2010;35:8216–24.
- [125] Paek S, Lee MS, Kim K-R, Ahn D-H, Song K-M, Sohn S-H. Development of 100-kCi tritium transport vessel. *IEEE Trans Plasma Sci* 2010;38(3):278–83.
- [126] Lewis FA. The palladium–hydrogen system. *Platin Met Rev* 1982;26(1):20–7.
- [127] Kuji T, Uchida H, Sato M, Cui W. Thermodynamic properties of hydrogen in fine Pd powders. *J Alloy Compd* 1999;293–295:19–22.
- [128] Kuji T, Matsumura Y, Uchida H, Aizawa T. Hydrogen absorption of nanocrystalline palladium. *J Alloy Compd* 2002;330–332:718–22.
- [129] Suleiman M, Faupel J, Borchers C, Krebs HU, Kirchheim R, Pundt A. Hydrogen absorption behavior in nanometer sized palladium samples stabilised in soft and hard matrix. *J Alloy Compd* 2005;404–406:523–8.
- [130] Suleiman M, Jisrawi NM, Dankert O, Reetz MT, Bähtz C, Kirchheim R, Pundt A. Phase transition and lattice expansion during hydrogen loading of nanometer sized palladium clusters. *J Alloy Compd* 2003;356–357:644–8.
- [131] Wenefska K, Michalkiewicz B, Gong J, Tang T, Kalenczuk R, Chen X, Mijowska E. In situ deposition of Pd nanoparticles with controllable diameters in hollow carbon spheres for hydrogen storage. *Int J Hydrog Energy* 2013;38:16179–84.
- [132] Chen C, et al. Hydrogen storage performance in palladium-doped graphene/carbon composites. *Int J Hydrog Energy* 2013;38:3681–8.
- [133] Dibandjo P, et al. Hydrogen storage in hybrid nanostructured carbon/palladium materials: influence of particle size and surface chemistry. *Int J Hydrog Energy* 2013;38:952–65.
- [134] Reddy GLN, Kumar S. Reversible hydrogen storage in vapour deposited Mg-5 at% Pd powder composites. *Int J Hydrog Energy* 2014;39:4421–6.
- [135] Kaminska A, Diduszko R, Czerwosz E, Kowalska E, Kozłowski M. Nanostructured C-Pd films for hydrogen applications. *Int J Hydrog Energy* 2014;39:9854–8.
- [136] Yuan J, Zhu Y, Li Y, Zhang L, Li L. Effect of multi-wall carbon nanotubes supported palladium addition on hydrogen storage properties of magnesium hydride. *Int J Hydrog Energy* 2014;39:10184–94.
- [137] US department of energy (DOE). Tritium handling and safe storage. DOE-HDBK-1129-2008 ;December 2008, p. 18–19.
- [138] Wang H, Gao Q, Hu J. High hydrogen storage capacity of porous carbons prepared by using activated carbon. *J Am Chem Soc* 2009;131(20):7016–22.
- [139] Xiao Y, Dong H, Long C, Zheng M, Lei B, Zhang H, Liu Y. Melaleuca bark based porous carbons for hydrogen storage. *Int J Hydrog Energy* 2014;39:11661–7.
- [140] Zhao W, Fierro V, Fernández-Huerta N, Izquierdo MT, Celzard A. Hydrogen uptake of high surface area-activated carbons doped with nitrogen. *Int J Hydrog Energy* 2013;38:10453–60.
- [141] Tellez-Jua rez MC, Fierro V, Zhao W, Fernández-Huerta N, Izquierdo MT, Reguera E, Celzard A. Hydrogen storage in activated carbons produced from coals of different ranks: effect of oxygen content. *Int J Hydrog Energy* 2014;39:4996–5002.
- [142] Weitkamp J, Fritz M, Ernst S. Zeolites as media for hydrogen storage. *Int J Hydrog Energy* 1995;20(12):967–70.
- [143] Anderson PA. Storage of hydrogen in zeolites. In: Walker G, editor. *Solid-state hydrogen storage: materials and chemistry*. Cambridge, UK: Woodhead Publishing Limited; 2008. p. 223–60.
- [144] Langmi HW, et al. Hydrogen adsorption in zeolites A, X, Y and RHO. *J Alloy Compd* 2003;256–357:710–5.
- [145] Langmi HW, et al. Hydrogen storage in ion-exchanged zeolites. *J Alloy Compd* 2005;404–406:637–42.
- [146] Li Y, Yang RT. Hydrogen storage in low silica type X zeolites. *J Phys Chem B* 2006;110(34):17175–81.
- [147] Azzouz A. Achievement in hydrogen storage on adsorbents with high surface-to-bulk ratio—prospects for Si-containing matrices. *Int J Hydrog Energy* 2012;37:5032–49.
- [148] Kleperis J, Lesnicenoks P, Grinberg L, Chikvaidze G, Klavins J. Zeolite as material for hydrogen storage in transport applications. *Latvian J Phys Techn Sci* 2013;50(3):59–64.
- [149] Grzech A, Yang J, Glazer PJ, Dingemans TJ, Mulder FM. Effect of long range van der Waals interactions on hydrogen storage capacity and heat of adsorption in large pore silicas. *Int J Hydrog Energy* 2014;39:4367–72.
- [150] Lototsky MV, Yartys VA, Pollet BG, Bowman Jr. RC. Metal hydride hydrogen compressors: a review. *Int J Hydrog Energy* 2014;39:5818–51.
- [151] Li L, Xu C, Chen C, Wang Y, Jiao L, Yang H. Sodium alanate system for efficient hydrogen storage. *Int J Hydrog Energy* 2013;38:8798–812.
- [152] Liang C, Liu Y, Fu H, Ding Y, Gao M, Pan H. Li–Mg–N–H-based combination systems for hydrogen storage. *J Alloy Compd* 2011;509:7844–53.
- [153] Graetz J, et al. Aluminum hydride as a hydrogen and energy storage material: past, present and future. *J Alloy Compd* 2011;509S:S517–28.
- [154] Goldsmith J, Wong-Foy AG, Cafarella MJ, Siegel DJ. Theoretical limits of hydrogen storage in metal–organic frameworks: opportunities and trade-offs. *Chem Mater* 2013;25(16):3373–82.
- [155] Tranchemontagne Dj, Park KS, Furukawa H, Eckert J, Knobler CB, Yaghi OM. Hydrogen storage in new metal–organic frameworks. *J Phys Chem C* 2012;116:13143–51.
- [156] Belof JL, Stern AC, Eddaoudi M, Space M. On the mechanism of hydrogen storage in a metal–organic framework material. *J Am Chem Soc* 2007;129:15202–10.
- [157] Collins Dj, Zhou HC. Hydrogen storage in metal–organic frameworks. *J Mater Chem* 2007;17:3154–60.